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SOLID WATER-IN-OIL EMULSION COSMETICS

Inventor:

Toshiaki Sugizaki
Kose Kenkyusho
48-18 Sakae
Kitaku, Tokyo

Applicant:

000145862
Kose Corp.
3-6-2 Nihonbashi
Chuoku, Tokyo

Agents:

Miyuki Ariga, patent
attorney, and 2 others

[Attached amendments have been incorporated into text of
translation.]

Abstract

Constitution

Solid water-in-oil type emulsion cosmetics containing the components (a) - (d) below:

- (a) Oily gel composition from oils and oil thickening agents;
- (b) Silicone gel composition and/or paste silicone composition;
- (c) polyoxyethylene sorbitan fatty acid ester;
- (d) water.

Effect

Hard gel to a solid state is obtained without the drawbacks of conventional water-in-oil creams such as heavy spreading, tackiness, oiliness.

Claim

Solid water-in-oil type emulsion cosmetics, characterized by containing the components (a)-(d) below:

- (a) Oily gel composition from oils and oil thickening agents;
- (b) Silicone gel composition and/or paste silicone composition;
- (c) polyoxyethylene sorbitan fatty acid ester;
- (d) water.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns solid water-in-oil emulsion type cosmetics, more specifically, concerns hard gel to solid state water-in-oil emulsion cosmetics with improvements in the properties of heavy spreading, tackiness, oiliness.

[0002]

Prior art and problems to be solved by the invention

In general, regardless of emulsion type (oil-in-water, water-in-oil, combinations of both), the emulsion bases display a soft paste state (so-called creamy) and lack uniqueness and novelty.

[0003]

The water-in-oil type creams are superior to oil-in-water type creams in skin protection effects, softening effects, moisture retention effects, etc.

[0004]

However, such water-in-oil type creams have disadvantages of heavy spreading, stickiness, oiliness, etc., and development of products free from such disadvantages is highly desired.

[0005]

Means to solve the problems

As a result of an intense study under such circumstances, we have discovered that water-in-oil type emulsion cosmetics with significantly reduced problems of heavy spreading of the solid or gel, tackiness, oiliness, etc., can be obtained by emulsification dispersion of an oily gel composition, silicone gel composition, certain fatty acid esters, and water. Thus, the present invention is attained.

[0006]

Namely, the present invention aims to provide solid water-in-oil type emulsion cosmetics, characterized by containing the components (a) - (d) below:

(a) Oily gel composition from oils and oil thickening agents;

- (b) Silicone gel composition and/or paste silicone composition;
- (c) polyoxyethylene sorbitan fatty acid ester;
- (d) water.

[0007]

The oils of component (a) that can be used in the present invention can be chosen without any restriction from those usually used in cosmetics, such as mineral oils, vegetable oils, animal oils, fatty acids, fatty acid esters, higher alcohols, more specifically, mineral oils such as liquid paraffin, petrolatum, solid paraffin waxes, ceresin wax, microcrystalline wax, etc.; animal and vegetable oils such as squalane, lanolin, castor oils, hydrogenated castor oil, olive oil, jojoba oil, macadamia nut oil, mink oil, turtle oil, almond oil, safflower oil, avocado oil, carnauba wax, candelilla wax, beeswax, japan wax, spermaceti wax, etc.; synthetic oils such as polyethylene wax, ethylene-propylene copolymers, etc.; fatty acids such as oleic acid, stearic acid, lauric acid, myristic acid, etc.; fatty acid esters such as isopropyl myristate, isopropyl palmitate, octyldecyl myristate, cetyl 2-ethylhexanoate, 2-ethylhexanoic acid triglyceride, glyceryl trioctanoate, diglyceryl isostearate, propylene glycol dicaproate, pentaerythritol rosinate, dipentaerythritol fatty acid esters, etc.; higher alcohols such as oleyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, etc. They may be used singly or as mixtures thereof.

[0008]

The oil thickening agents of component (a) include metallic soaps such as aluminum stearate, magnesium stearate, etc.; polysaccharide fatty acid esters such as sucrose palmitate, starch palmitate, ophiopogon [transliteration] stearate, etc.; organic-modified clay minerals such as dioctadecyldimethylammonium salt-modified montmorillonite, dihexadecyldimethylammonium salt-modified montmorillonite, etc.

[0009]

The content of the oil thickening agents in the oily gel compositions (a) is, but not limited to, 8-30 wt% (hereafter referred to simply %), while the compounding ratio of the oily gel composition (a) in the cosmetics of the present invention should be 30-70%. Below 30%, it is difficult to maintain the hard gel to solid state, while above 70%, excessive hardness makes the handling difficult and spreading too heavy.

[0010]

The silicone gel compositions of component (b) include those obtained, e.g., by kneading and swelling of partially crosslinked organopolysiloxane polymers and low-viscosity silicone oils.

[0011]

The partially crosslinked organopolysiloxane polymers used in component (b) of the present invention can be obtained, e.g., by crosslinking organopolysiloxanes to obtain organopolysiloxane polymers that are insoluble in benzene and contain benzene in amount more than their own weight and have three-dimensional crosslinked structures in some portions.

[0012]

Such polymers may contain R_2SiO units and $RSiO_{1.5}$ units or $R_3SiO_{0.5}$ units and/or SiO_2 units. They are insoluble in benzene and have a three-dimensional crosslinked structure containing benzene in an amount more than their own weight, and to maintain such conditions, the $RSiO_{1.5}$ units and/or SiO_2 units and R_2SiO units and/or $R_3SiO_{0.5}$ units should be in certain range. With $RSiO_{1.5}$ and/or SiO_2 unit content too small, the organopolysiloxane polymers do not have a sufficient three-dimensional crosslinked structure and are soluble in benzene, and they cannot be used even when they have apparent crosslinked structures. On the other hand, when the $RSiO_{1.5}$ units and/or SiO_2 units content is excessive compared with R_2SiO units and/or $R_3SiO_{0.5}$, the organopolysiloxane polymer has an excessive crosslinked structure, and while insoluble in benzene, the benzene content would be less than its own weight; thus, upon being mixed with low-viscosity silicone oils, the swelling of the organopolysiloxane polymers is not sufficient, resulting in separation and discharge of silicone oils, making stability retention difficult during usage. Thus, to obtain soft silicone

gel compositions of good stability, in general, desirable results can be obtained at (R_2SiO unit and/or $R_3SiO_{0.5}$ unit) : ($RSiO_{1.5}$ unit and/or SiO_2 unit) ratio in the 1:1-30:1 range (this may be affected also by the molecular weight of the polymers). In the above structural units, R may be an alkyl group such as hydrogen atom, methyl group, ethyl group, propyl group, etc.; aryl group such as phenyl group, tolyl group, etc.; unsaturated aliphatic group such as vinyl group, etc., and they may be the same or different.

[0013]

Such organopolysiloxane polymers insoluble in benzene and having three-dimensional crosslinked structures that can contain benzene in an amount above their own weight can be synthesized by various methods shown below:

i) Dehydrogenation reaction and condensation reaction by heating organopolysiloxane having at least two hydrogen atoms bonded to a silicon atom in the molecule in the presence of an alcoholic aqueous solution of a catalytic amount of alkali metal hydroxide;

ii) Dehydrogenative condensation reaction by heating organohydrogen polysiloxane having at least two hydrogen atoms bonded to a silicon atom in the molecule and organopolysiloxanes having at least two hydroxy groups bonded to a silicone atom in the molecule, in the presence of a catalytic amount of alkali metal hydroxide, platinum compound, etc.;

iii) Dehydrative condensation reaction by heating organopolysiloxane having at least two hydroxy groups bonded to

silicon in the molecule in the presence of a catalytic amount of alkali metal hydroxide, organotin compound, etc.;

iv) Alcohol removal reaction by heating organopolysiloxane having at least two hydroxy groups bonded to silicon atom in the molecule and organopolysiloxane having at least two alkoxy groups [bonded] to silicon atom in the molecule in the presence of a catalytic amount of alkali metal hydroxide, organotin compound, etc. In all the methods, the organopolysiloxane polymers obtained are insoluble in benzene and three-dimensional crosslinked structures that can contain benzene in an amount above their own weight.

[0014]

Other examples of such partially crosslinked organopolysiloxane polymers include organopolysiloxane polymers that are insoluble in silicone oils, but swell sufficiently and can be obtained by addition polymerization of (A) organohydrogen polysiloxanes and (B) aliphatic unsaturated group-containing organopolysiloxanes and have three-dimensional crosslinked structures in [certain] portions. The molecular structures of the organopolysiloxanes of (A) and (B) used here may be linear, branched, or cyclic, while linear ones are preferred for control of the synthetic reaction of the desired organopolysiloxane polymers. It is essential that the reactive groups, namely, (A) the hydrogen atoms bonded to the silicon atom in the organopolysiloxanes and (B) the aliphatic unsaturated group in the aliphatic unsaturated group-containing organopolysiloxanes should be two each per molecule for obtaining organopolysiloxane polymers having three-dimensional crosslinked structures in some

portions. Such reactive groups may be present in any position within a molecule either inside the molecular chains or at chain ends. The contents of such reactive groups in the organopolysiloxanes for obtaining soft silicone gel compositions with good stability should be 1-20 mol% in the case of linear or branched molecular structures and 1-50 mol% in the case of cyclic molecular structures. With the content exceeding the range, hard polymers are obtained which tend to have difficulty in containing the low-viscosity silicone oils inside the three-dimensional crosslinked structures, and separation and discharge occur, leading to poor stability. On the other hand, below this range, silicone gel compositions tend to lack the structural viscosity.

[0015]

The organohydrogen polysiloxanes of (A) comprise $\text{HSiO}_{1.5}$ units, $\text{RSiO}_{1.5}$ units, RHSiO units, R_2SiO units, $\text{R}_2\text{HSiO}_{0.5}$ units, $\text{R}_3\text{SiO}_{0.5}$ units, etc., wherein R represents alkyl groups such as methyl group, ethyl group, propyl group, butyl group, etc.; aryl groups such as phenyl group, tolyl group, etc.; cyclohexyl group, and substituted or unsubstituted monovalent hydrocarbon groups derived from the above groups with substitution of one or more of carbon-bonded hydrogen atoms by halogen atoms, cyano groups, other groups except aliphatic unsaturated groups such as vinyl group, etc. Representative examples are methyl hydrogen polysiloxanes containing $(\text{CH}_3)_3\text{SiO}^-$, $-[(\text{CH}_3)_2\text{SiO}]_p^-$, $-[\text{CH}_3\text{HSiO}]_q^-$, $-\text{Si}(\text{CH}_3)_3$ ($p = 10-500$; $q = 2-50$).

[0016]

The aliphatic unsaturated groups of the aliphatic unsaturated group-containing organopolysiloxanes of (B) are in general, vinyl group, allyl group, etc. The organovinylpolysiloxanes comprise $(CH_2=CH)SiO_{1.5}$ units, $RSiO_{1.5}$ units, $R(CH=CH_2)SiO$ units, R_2SiO units, $R_2(CH=CH_2)SiO_{0.5}$ units, $R_3SiO_{0.5}$ units, etc., wherein R is the same as defined above for (A). Representative examples are methyl vinyl polysiloxanes containing units of $(CH_2=CH)(CH_3)_2SiO-$, $-[(CH_3)_2SiO]_r-$ and $-Si(CH_3)_3(CH=CH_2)$ ($r = 10-100$), or units of $(CH_3)_3SiO-$, $-[(CH_3)_2SiO]_m-$, $-[(CH=CH_2)CH_3SiO]_n$, and $-Si(CH_3)_3$ ($m = 10-500$; $n = 2-50$). They may be used singly or as mixtures thereof.

[0017]

The addition reaction of such (A) organohydrogen polysiloxanes and (B) aliphatic unsaturated group-containing organopolysiloxanes can be carried out by a conventional manner. For example, corresponding organohydrogen polysiloxanes and organovinyl polysiloxanes are compounded at the silicon atom-bonded hydrogen and vinyl group molar ratio 1/3 to 3/1 and heated under stirring in the presence of an addition polymerization catalyst such as platinum or palladium. Using chloroplatinic acid described in Japanese Kokoku Patent No. Sho 33 [1958]-9969 as the addition polymerization catalyst is especially preferred.

[0018]

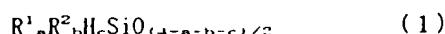
The low-viscosity silicone oils used as component (b) should be, but not restricted to, those having a viscosity about 50 cs or less. It is due to the fact that as viscosity increases, with a usage in large amounts, oiliness increases, resulting in poor feel of use. Thus, low-viscosity silicone oils should have a low degree of polymerization, such as dimethyl polysiloxanes, methyl phenyl polysiloxanes, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, etc. If needed, they may be used in mixtures of two or more.

[0019]

The paste silicone compositions of component (b) include the above low-viscosity silicone oils in the silicone polymers described below.

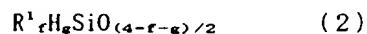
[0020]

The paste silicone compositions used in component (b) of the present invention are novel and contain organohydrogen polysiloxanes of the general formula (1):



(In the formula, R^1 independently represents substituted or unsubstituted alkyl group of 1-18 carbon atoms, aryl group, aralkyl group, or halo hydrocarbon group; R^2 represents polyoxyalkylene group of the general formula

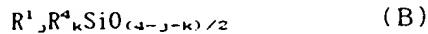
$C_nH_{2n}O(C_2H_4O)_d(C_3H_6O)_eR^3$ (R^3 represents hydrogen atom or C_{1-10} saturated aliphatic hydrocarbon group or $-(CO)R^5$ (R^5 represents C_{1-5} saturated aliphatic hydrocarbon group); d is a whole number of 2-200; e is a whole number of 0-200; $d + e$ is a whole number of 3-200; n is 2-6), a is 1.0-2.5; b is 0.001-1.0, c is 0.001-1.0) and/or organohydrogen polysiloxanes of the general formula (2) :



(In the formula, R^1 is as defined above; f is 1.0-3.0; g is 0.001-1.5) and polyoxyalkylene of the general formula (A) :



(In the formula, h is a whole number of 2-200; i is a whole number of 0-200; $h+i$ is a whole number of 3-200; m is 2-6) and/or organopolysiloxanes of the general formula (B) :



(In the formula, R^1 is as defined above; R^4 is a C_{2-10} monovalent hydrocarbon group having an aliphatic unsaturated group at chain end; j is 1.0-3.0; k is 0.001-1.5), wherein a composition of the combined weight of 100 parts by weight of the essential components of the above general formula (1) and/or the general formula (A) is subjected to addition polymerization in the presence or absence of 3-200 parts by weight of low-viscosity silicone oil of viscosity 100 cs or less at 25°C and/or polyhydroxy alcohols to obtain a silicone polymer, 100 parts by weight of which are kneaded under a shear force with 5-1000

parts by weight low-viscosity silicone oil to obtain the paste silicone compositions.

[0021]

While the silicone polymers in the paste silicone compositions of component (b) of the present invention are obtained by addition polymerization of organohydrogen polysiloxanes and aliphatic unsaturated group-containing compounds in the presence or absence of silicone oils of viscosity 100 cs or less at 25°C and/or polyhydroxy alcohols, the organohydrogen polysiloxane and/or the unsaturated group-containing compounds must contain a polyoxyalkylene group.

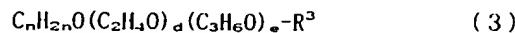
[0022]

Therefore, for example, in the combination of an organohydrogen polysiloxane and an aliphatic group-containing compound, the organohydrogen polysiloxane contains a polyoxyalkylene group of the general formula (1):



wherein R^1 are independently C_{1-18} substituted or unsubstituted alkyl group, aryl group, aralkyl group, halo hydrocarbon group chosen from an alkyl group such as methyl group, ethyl group, propyl group, butyl group, etc.; aryl group such as phenyl group, tolyl group, etc.; aralkyl group such as benzyl group, phenethyl group, etc.; the above groups in which carbon-bonded hydrogen atoms are partially or wholly substituted by halogen

atoms, such as chloromethyl group, trifluoropropyl group, etc.; R^2 are independently polyoxyalkylene groups of the general formula (3):



wherein R^3 is hydrogen atom or a C_{1-10} saturated hydrocarbon group such as methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, etc., or $-(CO)-R^5$; R^5 is a C_{1-5} saturated aliphatic hydrocarbon group; d is a whole number of 2-200; e is a whole number of 0-200; $d + e$ is a whole number of 3-200; n is 2-6.

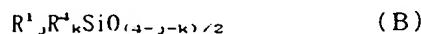
[0023]

With the a of the a , b and c values being below 1.0, the polymers obtained do not swell sufficiently by the silicone oils, while above 2.5, water cannot be dispersed sufficiently in the paste compositions obtained by kneading the polymers with silicone oils under shear force; thus, a should be 1.0-2.5, preferably 1.0-2.0. With b being below 0.001, water cannot be dispersed sufficiently in the paste compositions obtained by kneading the polymers obtained with silicone oils under shear force, while above 1.0, the polymer does not have sufficient swelling by the silicone oils; thus, b should be 0.001-1.0, preferably 0.005-1.0. With c being below 0.001, the polymers obtained by the addition polymerization show difficulty in forming three-dimensional structures and lack thickening properties for the silicone oils, while above 1.0, the addition polymerization produces excessive crosslinking density of the

three-dimensional structure, resulting in poor retention of silicone oils. Thus, c should be 0.001-1.0, preferably 0.005-1.0.

[0024]

In the organopolysiloxanes of general formula (B) combined with the unsaturated group-containing organohydrogen polysiloxanes of general formula (1):



with R^1 being same as defined above and R^4 C₂₋₁₀ monovalent hydrocarbon group having terminal aliphatic unsaturated groups such as vinyl group, allyl group, etc., if j is below 1.0, the three-dimensional structure crosslinking density in the polymers obtained by addition polymerization is excessive, and the polymers cannot retain the silicone oils in a stable manner, while above 3.0, the polymers obtained by the addition polymerization would have insufficient formation of three-dimensional structures, lacking the thickening properties for the silicone oils; thus, d should be in the range of 1.0-3.0, preferably 1.0-2.5. With k below 0.001, the desired polymers have difficulty in formation of three-dimensional structures and lack the thickening properties for the silicone oils, while above 1.5, the polymers obtained by addition polymerization have excessive three-dimensional structure crosslinking density and cannot retain the silicone oils in a stable manner; thus, k should be in the range of 0.001-1.5, preferably 0.005-1.0. The mixtures of the organohydrogen polysiloxanes of general formula

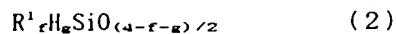
(1) and the organopolysiloxanes of general formula (B) will be referred to as mixture I hereafter.

[0025]

The organohydrogen polysiloxanes of general formula (1) can also be used in combination with the polyoxyalkylenes of general formula (A).

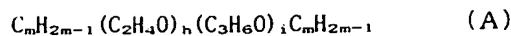
[0026]

In other combinations of such organohydrogen polysiloxanes with aliphatic unsaturated group-containing compounds, mixtures of the organohydrogen polysiloxanes of the general formula (2) can be used:



with R^1 being as defined above, wherein with f being below 1.0, the resulting polymers do not swell sufficiently with the silicone oils, while above 3, the polymers obtained by the addition polymerization have difficulty in three-dimensional structure formation and lack the thickening properties for the silicone oils; thus, f should be in the range of 1.0-3.0, preferably 1.0-2.5; with g being below 0.001, the polymers obtained by the addition polymerization have difficulty in forming three-dimensional structures and lack the thickening properties for the silicone oils, while above 1.5, the polymers obtained by the addition polymerization have excessive three-dimensional structure crosslinking density and cannot retain the

silicone oils in a stable manner; thus, g should be in the range of 0.001-1.5, preferably 0.005-1.0, and polyoxyalkylenes of the general formula (A) :



wherein h is 2-200, preferably 5-100; i is 0-200, preferably 0-100, while h/i should be 1 or higher for sufficient dispersion of water in the polymers obtained; m is 2-6, preferably 3-6. This mixture is referred to as mixture II hereafter.

[0027]

The low-viscosity silicone oils having a viscosity of 100 cs or less at 25°C, which are to be used in the addition polymerization of mixture I or mixture II in the present invention may be linear or branched dimethyl polysiloxane, methyl phenyl polysiloxane, ethyl polysiloxane, ethyl methyl polysiloxane, ethyl phenyl polysiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, etc. Any of these having a viscosity of 100 cs or less at 25°C can be used, while those having a viscosity of 50 cs or less are preferred. They may be used singly or as mixtures thereof.

[0028]

The polyhydroxy alcohols are, e.g., ethylene glycol, 1,3-butylene glycol, propylene glycol, dipropylene glycol, glycerol, diglycerol, etc. They may be used singly or as mixtures thereof.

[0029]

Based on 100 parts by weight of the mixture I or mixture II, the content of the low-viscosity silicone oil and/or polyhydroxy alcohols should be 3-200 parts by weight. Upon addition polymerization in the presence of such low-viscosity silicone oils and/or polyhydroxy alcohols, the polymers obtained contain such compounds and show superior swelling by silicone oils and thickening properties, compared with those obtained in the absence of them.

[0030]

The addition polymerization of the mixture I or mixture II can be carried out at room temperature or at 50-150°C in the presence of known platinum compound or rhodium compound catalysts such as chloroplatinic acid, alcohol-modified chloroplatinic acid or chloroplatinic acid-vinylsiloxane complexes.

[0031]

If needed, organic solvents may be used, e.g., aliphatic alcohols such as methanol, ethanol, 2-propanol, butanol, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; aliphatic or alicyclic hydrocarbons such as n-pentane, n-hexane, cyclohexane, etc.; halohydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, trichloroethane, trichloroethylene, fluorochlorohydrocarbons, etc.

[0032]

The content of the partially crosslinked organopolysiloxanes in the above silicone gel compositions and the content of the silicone polymers in the above paste silicone compositions should be 10-30%.

[0033]

The content of the resulting silicone gel composition and/or paste silicone compositions (b) in the cosmetics of the present invention should be 10-40%, preferably 15-35%. Below 10%, the improvement in feel of use is not realized, while above 40%, maintaining the hard gel to solid state is difficult.

[0034]

The polyoxyethylene sorbitan fatty acid esters of component (c) are colorless to light-yellow liquid to paste nonionic surfactants, available under the trade names of Nikkol GO-4, GO-430, GO-440, GO-460, GL-1, GS-460 (all products of Nippon Surfactant Kogyo Co.). Such polyoxyethylene sorbitan fatty acid esters (c) have an HLB value of 4 or higher, preferably 10-16. When such compounds (c) are used in mixtures, such mixtures should have HLB values in that range.

[0035]

The content of the polyoxyethylene sorbitan fatty acid esters (c) in the cosmetics of the present invention should be 0.5-5%. Below 0.5%, effects of the present invention are not realized, while above 5%, no additional benefits are obtained, and the feel of use is made worse.

[0036]

The content of the water of component (d) in the cosmetics of the present invention should be 5-35%. Below 5%, no feel of use improvements are realized, while above 35%, stability over time deteriorates. Component (d) may be compounded with aqueous components commonly used in cosmetics.

[0037]

The solid water-in-oil emulsion type cosmetics of the present invention can be prepared by the emulsion dispersion of water (d) using the polyoxyethylene sorbitan fatty acid esters (c) into mixtures of the oily gel compositions (a) and silicone gel compositions or paste silicone compositions (b).

[0038]

Beside the above components (a)-(d), the solid water-in-oil emulsion type cosmetics of the present invention may also contain within the scope of the present invention other common additives used for cosmetics, such as humectants, antiseptics,

antioxidants, UV absorbers, emollients, beauty components, perfumes, water-soluble polymers, protective pigments, coloring pigments, glittering pigments, organic powders, hydrophobically treated pigments, tar colors, etc.

[0039]

Effect of the invention

The solid water-in-oil emulsion type cosmetics of the present invention display a unique hard gel to solid state and overcome all the problems of heavy spreading, tackiness, oiliness, etc., encountered in conventional water-in-oil creams.

[0040]

Application examples

Next, the present invention is explained in detail with application examples. However, the present invention is not limited to such application examples.

[0041]

Reference Example 1

Synthesis of partially crosslinked organopolysiloxane polymers

Trimethylsilyl-terminated dimethyl methyl hydrogen polysiloxane (molecular weight 2300; CH_3HSiO to $(\text{CH}_3)_2\text{SiO}$ ratio

1:4 (molar)) was treated with 1% potassium hydroxide solution (ethanol to water ratio 2:1) and heated under reflux for polymerization. The formed reaction product was washed with water to remove the alkali and allowed to dry to obtain a benzene-insoluble organopolysiloxane polymer that can contain benzene amounting to 180% of its own weight.

[0042]

Reference Example 2

Synthesis of partially crosslinked organopolysiloxane polymers

In a planetary mixer of inner capacity 5 L, 1790 g trimethylsilyl-terminated dimethyl methyl hydrogen polysiloxane (average molecular weight 2340; Si-H 4.5 mol%) and 710 g dimethylvinylsilyl-terminated dimethyl polysiloxane (average molecular weight 930; vinyl group 7.7 mol%) were stir-mixed, followed by addition of 0.5 g 2% isopropanol solution of chloroplatinic acid, heating to 70-80°C, stirring for 2 h, reducing the system pressure to 5-10 mmHg, and stripping for 30 min to give a colorless soft solid organopolysiloxane polymer.

[0043]

Reference Example 3

Synthesis of partially crosslinked organopolysiloxane polymers

In a planetary mixer of inner capacity 5 L, 1790 g trimethylsilyl-terminated dimethyl methyl hydrogen polysiloxane (average molecular weight 2340; Si-H 4.5 mol%) and 4240 g dimethylvinylsilyl-terminated dimethyl methyl phenyl polysiloxane (average molecular weight 5560; vinyl group 1.5 mol%) were stir-mixed, followed by addition of 0.5 g 2% isopropanol solution of chloroplatinic acid, heating to 70-80°C, stirring for 2 h, reducing the system pressure to 5-10 mmHg, and stripping for 30 min to give a colorless soft solid organopolysiloxane polymer.

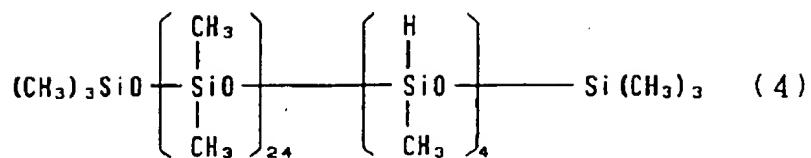
[0044]

Reference Example 4

(1) In a reactor, 68 g of organohydrogen polysiloxane of the average composition formula (4):

[0045]

[Structure 1]

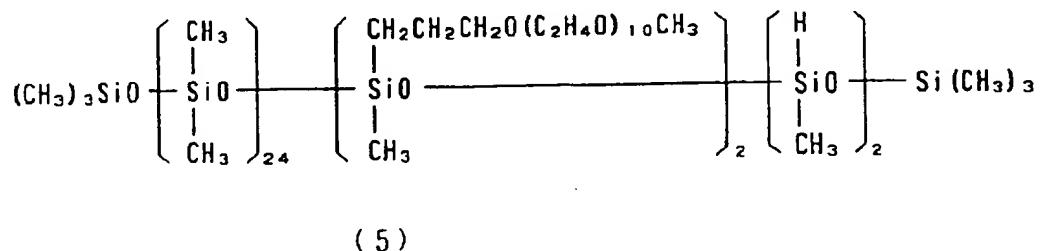


[0046]

100 g ethanol, 32 g polyoxyalkylene of the average composition formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{10}\text{CH}_3$, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, followed by stirring the resulting mixture for 2 h at internal temperature 70-80°C, removing the solvent in vacuo to obtain an organohydrogen polysiloxane of average composition formula (5):

[0047]

[Structure 2]

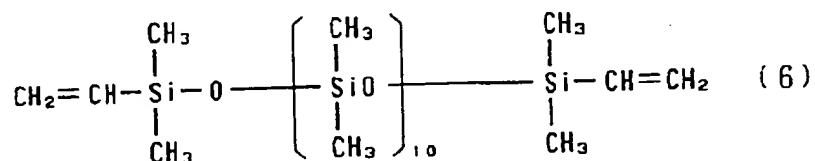


[0048]

(2) In a reactor, were placed 100 g of the organohydrogen polysiloxane obtained in (1), 100 g ethanol, 28.9 g dimethylvinylsilyl-terminated dimethyl polysiloxane of average composition formula (6):

[0049]

[Structure 3]



[0050]

and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, followed by stirring the resulting mixture at 70-80°C for 2 h, and stripping the solvent in vacuo to obtain an elastic polymer.

[0051]

A dispersed mixture of 20 parts by weight of the polymer obtained above and 80 parts by weight dimethyl polysiloxane (viscosity 6 cs) was kneaded sufficiently in a three-roll mixer under a shearing force to obtain a silicone composition

displaying a smooth feel and a uniform paste appearance with viscosity 32,000 cP.

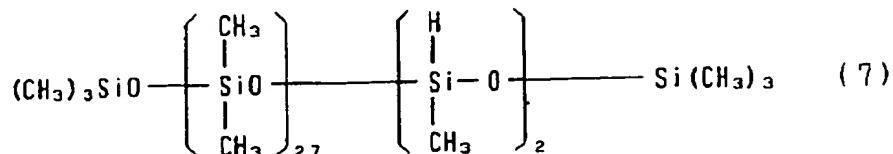
[0052]

Reference Example 5

In a reactor, 100 g organohydrogen polysiloxane of the average composition formula (7):

[0053]

[Structure 4]



[0054]

62 g ethanol, 23.6 g polyoxyalkylene of the average composition formula $\text{CH}_2=\text{CHCH}_2\text{O}-(\text{C}_2\text{H}_4\text{O})_{10}-\text{CH}_2\text{CH}=\text{CH}_2$ (8), and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, followed by stirring the resulting mixture at 70-80°C for 2 h, then stripping the solvent in vacuo to obtain a granular polymer.

[0055]

A dispersion mixture from 33 parts by weight of the above polymer obtained and 67 parts by weight dimethyl polysiloxane (viscosity 6 cs) was kneaded sufficiently under a shear force

using a three-roll mill to obtain a swollen silicone composition displaying a smooth feel and uniform paste appearance with viscosity 24,800 cP.

[0056]

Reference Example 6

In a reactor, 100 g organohydrogen polysiloxane of the average composition formula (4) obtained in Reference Example 1, 75 g ethanol, 49.4 g of the polyoxyalkylene of the average composition formula (8) used in Reference Example 2, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, followed by stirring the resulting mixture at internal temperature 70-80°C for 2 h, then stripping the solvent in vacuo to obtain a granular polymer.

[0057]

A dispersion mixture from 33 parts by weight of the above polymer obtained and 67 parts by weight dimethyl polysiloxane (viscosity 6 cs) was kneaded sufficiently under a shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 10,600 cP.

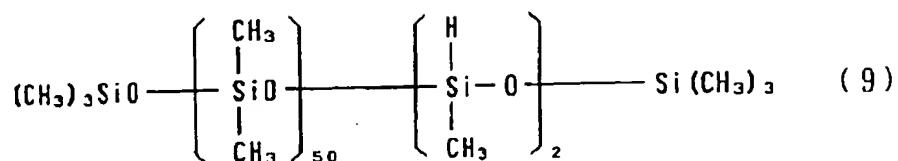
[0058]

Reference Example 7

In a reactor, 100 g of organohydrogen polysiloxane of the average composition formula (9):

[0059]

[Structure 5]



[0060]

57 g ethanol, 13.5 g of the polyoxyalkylene of the average composition formula (8) used in Reference Example 2, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, followed by heating the resulting mixture at 70-80°C for 2 h, then stripping the solvent to obtain a granular polymer.

[0061]

A dispersion mixture from 20 parts by weight of the above polymer obtained and 80 parts by weight dimethyl polysiloxane (viscosity 6 cs) was kneaded sufficiently under a shear force using a three-roll mill to obtain a swollen silicone

composition, displaying a smooth feel and uniform paste appearance with viscosity 22,800 cP.

[0062]

Reference Example 8

In a reactor, 100 g of the organohydrogen polysiloxane of the average composition formula (7) used in Reference Example 2, 103 g ethanol, 23.6 g of the polyoxyalkylene of the average composition formula (8) obtained in Reference Example 2, 82.4 g dimethyl polysiloxane of viscosity 6 cs at 25°C, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid at internal temperature 70-80°C for 2 h were stirred, followed by stripping the solvent in vacuo to obtain a silicone polymer.

[0063]

A dispersion mixture from 100 parts by weight of the above polymer obtained and 100 parts by weight dimethyl polysiloxane having viscosity 6 cs at 25°C was kneaded sufficiently under a shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 82,800 cP.

[0064]

Reference Example 9

In a reactor, 100 parts by weight of organohydrogen polysiloxane of the average composition formula (9) obtained in Reference Example 4, 95 g ethanol, 13.5 g of the polyoxyalkylene of the average composition formula (8) used in Reference Example 2, 75.7 g dimethyl polysiloxane having viscosity 5 cs at 25°C, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were processed similarly as in Reference Example 5 to obtain a polymer.

[0065]

A dispersion mixture from 100 parts by weight of the above polymer obtained and 200 parts by weight of octamethylcyclotetrasiloxane was kneaded sufficiently under shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 44,000 cP.

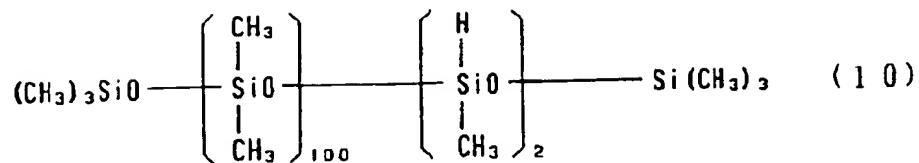
[0066]

Reference Example 10

In a reactor, 100 g of the organohydrogen polysiloxane of the average composition formula (10) :

[0067]

[Structure 6]



[0068]

74 g ethanol, 18.5 g polyoxyalkylene of the average composition formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{30}\text{CH}_2\text{CH}=\text{CH}_2$ (11), 29.6 g dimethyl polysiloxane of viscosity 6 cs at 25°C, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were placed, and the resulting mixture was processed similarly as in Reference Example 5 to obtain a polymer.

[0069]

A dispersion mixture from 100 parts by weight of the above polymer obtained and 200 parts by weight phenyl tris(trimethylsiloxy)silane was kneaded sufficiently under a shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 25,500 cP.

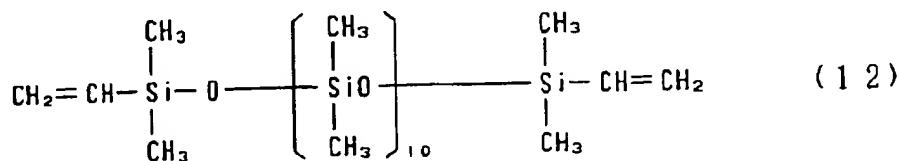
[0070]

Reference Example 11

In a reactor, 100 g of organohydrogen polysiloxane of the average composition formula (5) obtained in Reference Example 1 (1), 72 g ethanol, 28.9 g dimethylvinylsilyl-terminated dimethyl polysiloxane of the average composition formula (12):

[0071]

[Structure 7]



[0072]

14.3 g dimethyl polysiloxane of viscosity 30 cs at 25°C, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were processed, similarly as in Reference Example 5 to obtain a polymer.

[0073]

A dispersion mixture from 22.2 parts by weight of the above polymer obtained and 77.8 parts by weight dimethyl polysiloxane having viscosity 6 cs at 25°C was kneaded sufficiently under a

shear force using a three-roll mill to obtain a silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 48,000 cP.

[0074]

Reference Example 12

In a reactor, 100 g of the organohydrogen polysiloxane of the average composition formula (7) used in Reference Example 2, 23.6 g of the polyoxyalkylene of the average composition formula (8) used in Reference Example 2, 82.4 g 1,3-butylene glycol, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were stirred at 70-80°C for 2 h, followed by stripping the solvent to obtain a silicone polymer.

[0075]

A dispersion mixture from 100 parts by weight of the above polymer obtained and 100 parts by weight dimethyl polysiloxane having viscosity 50 cs at 25°C was kneaded sufficiently under a shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 65,000 cP.

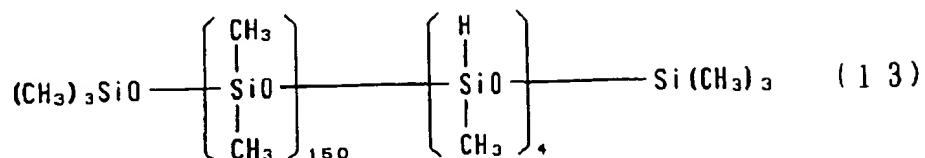
[0076]

Reference Example 13

In a reactor, 100 g of the organohydrogen polysiloxane of the average composition formula (13):

[0077]

[Structure 8]



[0078]

160 g ethanol, 34.7 g of polyoxyalkylene of the average composition formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{30-}(\text{C}_3\text{H}_6\text{O})_{10-}\text{CH}_2\text{CH}=\text{CH}_2$ (14), 20 g ethylene glycol, 13.7 g dimethyl polysiloxane of viscosity 10 cs at 25°C, and 0.3 g 3 wt% ethanol solution of chloroplatinic acid were processed, similarly as in Reference Example 5 to obtain a polymer.

[0079]

A dispersion mixture from 100 parts by weight of the above polymer obtained and 300 parts by weight decamethylcyclopentasiloxane was kneaded sufficiently under a

shear force using a three-roll mill to obtain a swollen silicone composition, displaying a smooth feel and uniform paste appearance with viscosity 52,000 cP.

[0080]

Application Examples 1-5, Comparative Examples 1-4

Solid water-in-oil emulsion cosmetics of the compositions shown in Table I (Application Examples 1-3, Comparative Examples 1-3) and Table II (Application Examples 4-5, Comparative Examples 4) were prepared according to the method given below:

[0081]

Preparation

- (A) (1) - (8) were heated for dissolution.
- (B) (A), (9) or (10) and (11) - (18) were heated for dissolution.
- (C) (19) and (20) were added to (B) with emulsification.
- (D) The resulting mixture was filled into a container to obtain products.

[0082]

The obtained products were allowed to stand in a thermostatic bath at 15°C for 1 day, 1 week, and 2 weeks and inspected for water separation in bulk or container bottom [sic], displaying a circle for no separation, triangle for some separation, and X for distinct separation for evaluation of the stability over time. Results are given in Tables I and II.

[0083]

Table I

(1) (重量%)

(4) 組成	(2) 実施例			(3) 比較例		
	1	2	3	1	2	3
(1) バクモンドウステアリン酸エステル	10.0	10.0	—	10.0	10.0	10.0
(2) デンブン脂肪酸エステル	—	—	10.0	—	—	—
(3) スクワラン	5.0	5.0	5.0	5.0	5.0	5.0
(4) トリオクタン酸グリセリル	10.0	10.0	10.0	10.0	10.0	10.0
(5) マカデミアンナッツ油	18.0	18.0	18.0	18.0	18.0	18.0
(6) セタノール	3.0	3.0	3.0	3.0	3.0	3.0
(7) コレスチロール	3.0	3.0	3.0	3.0	3.0	3.0
(8) ミンロウ	5.0	5.0	5.0	5.0	5.0	5.0
(9) シリコーンゲル組成物	20.0	—	—	20.0	20.0	20.0
(10) ベースト状シリコーン組成物	—	20.0	20.0	—	—	—
(11) 防腐剤	0.1	0.1	0.1	0.1	0.1	0.1
(12) ポリオキシエチレン (30E.O.) ソルビットテトラオレエート (HLB:11.5)	1.0	1.0	1.0	—	—	—
(15) ポリオキシエチレン (20E.O.) モノオレイン酸ソルビタン (HLB:15.0)	—	—	—	1.0	—	—
(16) ポリオキシエチレン (40E.O.) 硬化ヒマシ油 (HLB:12.5)	—	—	—	—	1.0	—
(17) ポリオキシエチレン (20E.O.) セチルエーテル (HLB:17.0)	—	—	—	—	—	1.0
(19) グリセリン	5.0	5.0	5.0	5.0	5.0	5.0
(20) 精製水	(10) 残量	残量	残量	残量	残量	残量
(6) 経時安定性	1日後 (7)	○	○	○	○	○
	1週間後 (8)	○	○	○	×	×
	2週間後 (9)	○	○	○	—	—

Key: 1 (wt%)
2 Application Example
3 Comparative Example
4 Composition
5 Ophiopgon stearate
Starch fatty acid ester
Squalane
Glyceryl trioctanoate
Macadamia nut oil
Cetanol
Cholesterol
Beeswax
Silicone gel composition
Paste silicone composition
Antiseptic
Polyoxyethylene(30E.0) sorbitan tetraoleate (HLB 11.5)
Polyoxyethylene(20E.0) sorbitan monooleate
Polyoxyethylene(40E.0) cured castor oil
Polyoxyethylene(20E.0) cetyl ether
Glycerol
Purified water
6 Stability over time
7 After 1 day
8 After 1 week
9 After 2 weeks
10 Balance

[0084]

Table II

②組成	③	③	① 重量%	④
	実施例4	実施例5	比較例4	
(1) バクモンドウステアリン酸エステル	10	10	10	
(3) スクワラン	5	5	5	
(4) トリオクタン酸グリセリル	10	10	10	
(5) マカデミアンナッツ油	18	18	18	
(6) セタノール	3	3	3	
(7) コレステロール	3	3	3	
(8) ミツロウ	5	5	5	
(9) シリコーンゲル組成物	20	20	20	
(11)防腐剤	0.1	0.1	0.1	
(13)ポリオキシエチレン(6E.O.)ソルビットモノラウレート(HLB:15.5)	1	—	—	
(14)ポリオキシエチレン(6E.O.)ソルビットテトラオレエート(HLB:8.5)	—	1	—	
(18)ポリオキシエチレン(4.2E.O.)ラウリルエーテル(HLB:8.0)	—	—	1	
(19)グリセリン	5	5	5	
(20)精製水	○	○	○	
⑥ 経時安定性	1日後 ⑦	○	○	○
	1週間後 ⑧	○	○	×
	2週間後 ⑨	○	△	—

Key: 1 wt%
2 Composition
3 Application Example
4 Comparative Example
5 Ophiopogon stearate
Squalane
Glyceryl trioctanoate
Macadamia nut oil
Cetanol
Cholesterol
Beeswax
Silicone gel composition
Antiseptic
Polyoxyethylene (6E.0) sorbitan monolaurate
Polyoxyethylene (6E.0) sorbitan tetraoleate
Polyoxyethylene (4.2E.0) lauryl ether
Glycerin
Purified water
6 Stability over time
7 After 1 day
8 After 1 week
9 After 2 weeks
10 Balance

[0085]

The silicone gel compositions (9) in Tables I and II were prepared by dispersion mixing, sufficient kneading and swelling from 25 parts by weight of the organopolysiloxane polymer obtained in Reference Example 2 and 75 parts by weight dimethyl polysiloxane having viscosity 10 cs at 25°C. The paste silicone composition (10) in Table I was prepared by dispersion mixing of 25 parts by weight of the silicone polymer obtained in Reference Example 8 and 75 parts by weight dimethyl polysiloxane having

viscosity 10 cs at 25°C, followed by sufficient kneading under a shear force using a three-roll mill and swelling.

[0086]

As shown clearly in Tables I and II, the products of the present invention (Application Example 1-5) have excellent stability over time.

[0087]

The products of Application Examples 1-3, commercial water-in-oil nourishing cream (Comparative Example 5), an commercial oil-in-water cream (Comparative Example 6) were subjected to functional tests for the items shown in Table III according to the methods and standards given below.

[0088]

Rheometer needle penetration

Evaluation method

Using a rheometer (product of Futo Kogyo), needle penetration was measured (diameter 1 cm, speed 6 cm/min, depth 1.5 mm, temperature 15°C)

Evaluation standard: numerical values of results.

[0089]

Solid form retention

Evaluation method

Inspected visually for sample in a metal tray at 50°C.

Evaluation standard: circle for solid form retention, and X for no retention.

[0090]

Ease of handling and feel of use

Evaluation method

Test was made with a 10-member expert panel, giving average subjective evaluation from each panel member.

Evaluation standard

Point 3 for very good, 2 for good, 1 for average, and 0 for not good, with circle for average point 2 or more, triangle above 1 but below 2, X for below 1.

[0091]

Table III

評価項目 (2)	(1) 製品	実施例 (5)			比較例 (6)	
		1	2	3	5	6
(3) 固さ	レオメータ (7) 針入度	108	102	98	38	10
	固型状の維持 (8)	○	○	○	×	×
	取れ易さ (9)	○	○	○	×	×
(4) 使用感	のびの良さ (10)	○	○	○	×	○
	油っぽさのなさ (11)	○	○	○	×	△
	べたつき感のなさ (12)	○	○	○	×	△
	保護効果の持続性 (13)	○	○	○	○	×

Key:

- 1 Products
- 2 Evaluation items
- 3 Hardness
- 4 Feel of use
- 5 Application Example
- 6 Comparative Example
- 7 Rheometer needle penetration
- 8 Solid form retention
- 9 Ease of handling
- 10 Good spreading
- 11 No oiliness
- 12 No tack
- 13 Protective effect retention

[0092]

As shown clearly in Table III, the products of the present invention (Application Example 1-3) have desirable hardness as well as good spreading and no oiliness and tack, yet excellent protective effect retention. On the other hand, the creams of Comparative Example 5 and 6 lacked the hard gel to solid form of the present invention, and they could not maintain the solid form at higher temperatures and did not provide good feel of use.